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## Synthesis and application of hydrophobized waxy potato starch

Miel, Jan Willem Johannes

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# Chapter 2

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## *Properties of benzylated native and oxidized waxy potato starch*

### **Abstract**

New benzylated products based on waxy potato starch and oxidized waxy potato starch were prepared and characterized. Characterization was performed on properties relevant for the replacement of styrene butadiene rubber (SBR) latex in high quality paper coatings. Waxy potato starch does not contain amylose, which may result in different product behavior than reported for normal potato starch or corn starch. The reaction was pseudo-zero order in benzyl chloride. The reaction efficiency was similar to values reported for normal potato- and corn starch. Both in case of native classic- as well as waxy potato starch, a dispersion was obtained upon cooking their benzylated products. The oxidized derivatives, however, showed a dramatic increase in the viscosity at a degree of substitution (DS)  $>0.3$ . Native waxy potato starch becomes insoluble at a DS of 0.375. The increased viscosity could be tuned by changing the level of oxidation. The pasting-peak of benzylated oxidized starches increased, while the onset temperature decreased. The surface tension of the dry starch films dropped from 57 to 43 mN/m after benzylation. The relative contribution of polar forces to the surface tension decreased. It was calculated that the work of adhesion between all benzylated starch products and cellulose decreases at increasing DS, which may be a drawback. Overall, increased hydrophobicity is assumed to be beneficial for the application in paper coatings.

**Key words:** *waxy potato starch, hydrophobic modification, benzylation, viscosity, surface tension*

### **Introduction**

Starch from different sources are used as functional ingredients in many applications and provide viscosity, texture, adhesion, appearance, etc., or a combination [1] of these features. For most applications (chemical) modification of the native types is required to some extent [2] to tailor

properties to specific product demands. Added functionality by modification may allow starch to be used as a renewable resource to replace functional, oil based polymers in a cost efficient way. One example is the paper industry, where cationic starch is an important ingredient in wet-end applications and oxidized starches are used in increasing amounts in coatings [3].

High quality paper coatings are applied for improved printing quality. Typically, such a coating is composed of a pigment, a binder and minor amounts of other additives [4]. The binder provides adhesion between the substrate and the coating components. Synthetic binders like (styrene butadiene rubber) SBR latex or natural binders such as starch are applied either solely or in a co-binder system [4].

SBR latex is a stable colloidal dispersion which is mainly composed of two hydrophobic monomers; styrene and butadiene [5]. The viscosity of latex is around 300 mPa.s at 50 %W solids content and displays shear thinning behavior. These are desirable properties for a common coating technique such as blade coating [6], which is operated at a speed of around 2000 m/min with shear rates exceeding  $10^7 \text{ s}^{-1}$ . For economic reasons, a total formulation solids content of about 70% is required at a viscosity of around 1000 mPa.s for good machine runability. After application, the coating formulation is dried at high temperature, close to the boiling point of water [7]. The whole process typically occurs in less than 5 seconds in which SBR latex is capable of forming a uniform, well adhering, porous surface in the form of a water resistant, flexible film with a low surface energy. This surface provides proper wettability for the oil, present in the ink used for off-set printing [8,9].

Starches on the other hand, are hydrophilic bio-macromolecules forming viscous gels in water after gelatinization and cooking, exceeding 300 mPa.s at a solids content of 5 %W. Starch films are expected to be more rigid, recrystallize over time (retrogradation) and have a higher surface energy than SBR latex due to the abundant presence of hydroxyl groups. Currently, oxidized starches are already applied in base- and mid-coatings. Sufficiently low paste viscosity at concentrations of at least 30 %W is realized by oxidation of classic native potato starch (PS) [10]. Replacement of synthetic binders by starch in paper coating formulations was found to have an effect on the entire downstream processing chain. The drying behavior changes [11] and, more importantly, the presence of starch has been linked to a common printing deficiency called mottling [12,13]. Migration of starch to the coating surface may occur during the drying process or as a result of subsequent wetting and drying either by application of new coating layers or during offset printing. Viscosity, surface tension and drying speed were used to model and describe the migration process [10,14-17].

Besides hypochlorite oxidation, benzylation of corn- and potato starch is reported in the patent literature for the replacement of SBR latex [19]. Benzylated starches yield a stable, latex-like, starch-based dispersion upon cooking with sub-micron particle size and decreased viscosity compared to native starch. Moreover, the formation of a water resistant, well adhering starch film was achieved. These properties were reported to be beneficial for the application of starch in paper coating formulations [18,19]. Many reports on hydrophobic modification of starch in general exist in the literature [20-24], however, none was investigated as thoroughly as benzylation. Gomberg and Buchler [25] first reported on benzylated carbohydrates in 1921 and since then optimization of the production process [19,26-28], kinetics [23,29] and substitution pattern [30] have been investigated. The viscosity of cooked pastes of benzylated starches is still too high for application in paper coatings, which can be concluded from the viscosities reported by Bohrisch et. al [27]. The decreased viscosity of benzylated starches may be the result of the formation of a dispersion. Part of the total starch solids content is held by the dispersed particles leaving less dissolved starch to contribute to the 'dispersion' viscosity. In the literature, however, it is also reported that the introduction of hydrophobic properties on a hydrophilic polymer increases the viscosity and may introduce a lower critical solution temperature (LCST) [31].

Waxy potato starch is a relatively new product [32,33]. Due to the absence of amylose, solutions based on waxy starch have increased stability and may form amorphous dry films. As far as the authors are aware, no reports on benzylation of waxy potato starch, or oxidized potato starches exist in the literature. This article reports on the investigation of the hypothesis that a combination of oxidation and hydrophobic modification by benzylation provides properties which should improve the performance of waxy potato starch in paper coating. This includes a sufficiently low solution viscosity, reduced water sensitivity to limit migration and a decreased film surface energy to improve oil wettability during off-set printing. Waxy potato starch (>99% amylopectine) and three grades of commercially available oxidized grades of waxy potato starch and native potato starch (20% amylose) were used as starting materials.

## ***Experimental***

### ***Materials***

Native potato starch, native waxy potato starch (>99% amylopectine) and oxidized waxy potato starches (Perfectafilm X115, X85 and X55) were kindly supplied by AVEBE Foxhol, The Netherlands, and were used as received. DMSO chromasolv-plus for HPLC >99.7% (Sigma) with 5 g/l LiBr (Sigma)

was used for GPC measurements to determine the starch molecular weight. Sodium hydroxide (Merck), benzyl chloride (Sigma), sodium sulfate (Sigma) and HCl (Merck) were used as received. For chemical analysis: Methanol (100%, Sigma) and Acetic acid (100%, Merck) were used as received. For contact angle measurement water, formamide (Sigma), diiodomethane (Sigma) and ethylene glycol (0% water, Sigma) were used as received.

### **Synthesis**

The synthesis of benzylated starch was performed according to Berkhout and Guns [19], with modifications. Starch was suspended in water containing 350 g/l of sodium sulfate at 35 °C and fed into a jacketed, stirred glass reactor in a 38 W% suspension, based on dry mass starch in water. 3 Grams of NaOH per mole anhydroglucose (AGU) was added drop wise as a 5 W% in water solution while vigorously stirring. The temperature was raised to 50°C. The required amount of benzyl chloride to obtain the desired (or theoretical maximum) degree of substitution ( $DS_{th}$ ) was added. DS will be used here to indicate the ratio between the moles benzyl chloride added per mole of AGU. An AGU unit has three hydroxyl groups available for substitution. By definition, the maximum DS is therefore 3. NaOH (5 W%) was added drop wise over 48h to a total of 1.05 mol NaOH per mole benzyl chloride. The reaction was allowed to proceed for a total of 72h after addition of benzyl chloride. Prior to washing, the reactor content was neutralized to pH 5-6 with 6 N HCl. The product was washed three times with demi water and three times with acetone to remove any residuals. Products were dried for at least 48h at 35°C and ground before storing.

### **Chemical characterization**

The DS was determined by UV-absorption according to Marsman et al. [34], with modifications. 5 gram of starch sample was washed with 50 ml methanol for 1 hour, decanted and dried at 105°C. The samples were dissolved in 50 ml of a 50/50- V/V mixture of 100% acetic acid and 0.2 M HCl at 95°C for 15 minutes while stirring. After cooling, the UV absorption was measured on a PE UV/Vis Lambda 12 spectrometer. The spectrometer was calibrated with benzyl-alcohol [35]. The reaction efficiency was calculated from the ratio  $DS_{UV} : DS_{th}$ .

### **Gelatinization behavior**

Gelatinization behavior of the products was recorded on a Newport Scientific Pty Ltd, Australia RVA-super4 Rapid Visco Analyzer. The samples were prepared at 20 W% dry solids of starch; the

native starch products were prepared at 5 W%. The heating and cooling cycle, also used by others [36], comprised of rapid stirring at 960 rpm for 10 seconds and subsequently 160 rpm for the remaining run time. Before heating, the sample was stirred for 2 minutes at 30°C. Next, the temperature profile was set to increase from 30 to 90 °C at 15°C/min. After a holding time of 4 minutes at 90°C, the sample was cooled back to 30 °C at 15°C/min. The measurement was allowed to proceed for 8 more minutes at 30°C.

### ***Solution preparation***

Solutions of starch were prepared by stirring a 15 %W (native) or 35 %W (oxidized) suspension, based on starch dry solids, in a hot-water-bath at 95°C for 30 minutes at 600 rpm with a six-hole lab-stirrer. Dilutions were prepared by adding warm demi water (>50°C). In some cases, the starch solution would foam upon cooking. The stirrer speed was adjusted in these cases.

### ***Solution viscosity: concentration and temperature dependence***

The viscosity of starch solutions was determined on a Haacke III rheometer using a cone – plate configuration at 20°C. The gap distance (d) was 0.105 mm, the cone diameter 60 mm and the angle 2°. Two ml of a starch solution was used and measured at 10 s<sup>-1</sup> shear rate. The viscosity as a function of temperature was determined between 20 and 70°C at a constant shear rate of 10 s<sup>-1</sup>. The viscosity was averaged over 5 seconds after 30 seconds of stabilizing.

### ***UV-emission spectroscopy***

The UV emission spectrum of pyrene in starch solutions was recorded on Fluorolog3-22 fluorescence spectrometer according to known literature [37]. The excitation wavelength was 334 nm at a slit width of 8 nm and the spectrum was recorded from 350-420 nm at a slit width of 2 nm. The ratio between the emission peak at 373 nm (I<sub>1</sub>) and 384 nm (I<sub>3</sub>) was calculated. A concentration of 2 µM pyrene was obtained by adding 8\*10<sup>-3</sup> W% pyrene in methanol to the samples.

### ***Molecular weight***

The molecular weight was determined on an Agilent Technologies 1260 infinity GPC-SEC system with DMSO containing 5 g/l LiBr to enhance gelatinization, according to Ciric et. al. [38]. The concentration of starch was set to 2 mg/ml. Starch samples were gelatinized in water and freeze-

dried after which the sample was stirred overnight in DMSO at room temperature, heated and stirred at 95°C for 2 hours and filtered over a 0.45 µm filter. The GPC system was equipped with a PFG guard-column and a G1362A 1260 RID Agilent Technologies RI detector. Samples were injected twice (1 µl) at a flowrate of 0.5 ml/min. The system was calibrated with Pullulan 800.

### Contact angle measurement

Starch films for contact angle measurement were prepared from a 3 W% solution. The solutions were dropped onto a 2 x 5 cm (b x l) glass plate and dried at ambient conditions for more than 48h. The surface energy was determined on a Dataphysics OCA 15 machine according to the method of Owens and Wendt [39]. Three liquids were applied; water, formamide and diiodomethane. The contact angle was averaged over 2 seconds at stable contact angle. In some cases, ethylene glycol was used to replace water if the contact angle would not stabilize. Five repetitions per liquid per sample were made. Samples were prepared in two fold. The surface tension of the starch products was used to predict the work of adhesion and the sensitivity to separation upon wetting [40]. The work of adhesion can be estimated by the Dupré relation (Equation 1):

$$W_{adh} = \gamma_{S_1} + \gamma_{S_2} - \gamma_{S_1S_2} \approx 2 \left[ (\gamma_{S_1}^d \gamma_{S_2}^d)^{1/2} + (\gamma_{S_1}^p \gamma_{S_2}^p)^{1/2} \right] \quad (\text{Equation 1})$$

$W_{adh}$  is the work required to separate surface 1 and 2,  $\gamma_i$  is the surface tension,  $S_1$  is solid 1 (in this case starch) and  $S_2$  is solid 2 (cellulose or  $\text{CaCO}_3$ ). Superscripts d and p represent the contribution of disperse- and polar forces to the total surface tension. For  $W_{adh} > 0$ , adhesion takes place and a higher value means that more energy is required to separate compounds 1 and 2. Equation 1 can be applied to indicate spontaneous separation of a polymer if submerged in a liquid. For  $S_1$  and  $S_2$  the interactions between the solid and the liquid ( $S_1L$  and  $S_2L$ ) are substituted, leading to Equation 2:

$$W_{adh} = \gamma_{S_1L} + \gamma_{S_2L} - \gamma_{S_1S_2} \quad (\text{Equation 2})$$

Here,  $\gamma_{S_1L}$  is the solid1-liquid interaction. Separation occurs if  $\gamma_{S_1S_2} > \gamma_{S_1L} + \gamma_{S_2L}$ .  $\gamma_{S_1L}$  was calculated from the contact angle results and by using Equation 3:

$$\gamma_{1,2} = \gamma_1 + \gamma_2 - \left[ 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} \right] \quad (\text{Equation 3})$$

Equation 3 is a general equation. In fact, the subscripts 1 and 2 may represent any compound, either a gas, solid or liquid.

## Results and discussion

Benzylated waxy potato starch derivatives were synthesized from starting materials with varying level of oxidation. The molecular weight of the starting materials is shown in Table 1. After washing and drying the product, chemical characterization by UV spectrometry was performed to determine the reaction efficiency. The pasting profile was recorded and the viscosity as a function of concentration and temperature was determined. Contact angle measurements provided data to calculate the surface tension including the polar and disperse contributions.

Starch <sup>a</sup>	M <sub>w</sub> (10 <sup>6</sup> )
Waxy potato (native)-0	30.2
X115-0	6.30
X85-0	2.60
X55-0	0.77

Table 1: molecular weight of starting materials.

a) “-0” indicates that the reported value is a property of the starting material, as received.

### Reaction

Unlike normal potato starch, native waxy potato starch did not turn yellow upon addition of NaOH, due to the lower amount of reducing ends in the waxy starch [41]. Oxidized waxy potato starches showed yellow-coloring; at increasing DS and level of oxidation, coloring increased. Upon neutralization, coloring decreased and most color was washed out. The products were all slightly yellow. After 24-48 hours, minor coagulation of granules occurred at the highest DS (0.3 and higher). A small fraction of the starch seemed to dissolve during the washing procedure since foam formation was observed, which was also reported in the literature [23]. At the last water-washing step, the products at a DS > 0.2 showed decreased filterability. Minor swelling of granules based on oxidized starch was observed upon the addition of acetone at the first wash. This effect may be explained by the increased solubility of benzylated starch towards organic liquids as reported by Hamilton and Yanovsky [42]. Up to a DS of 0.375, the granules of the oxidized and benzylated starches showed minor damage and occasional swelling or gelatinization, but did not lose their crystallinity as a consequence of the rather severe reaction conditions. In Figure 1 the difference between X85-0 and X85-0.375 (X85 with a DS of 0.375) is shown. The Maltese cross was observed with cross-polarized light under the microscope for all products listed in Table 2.



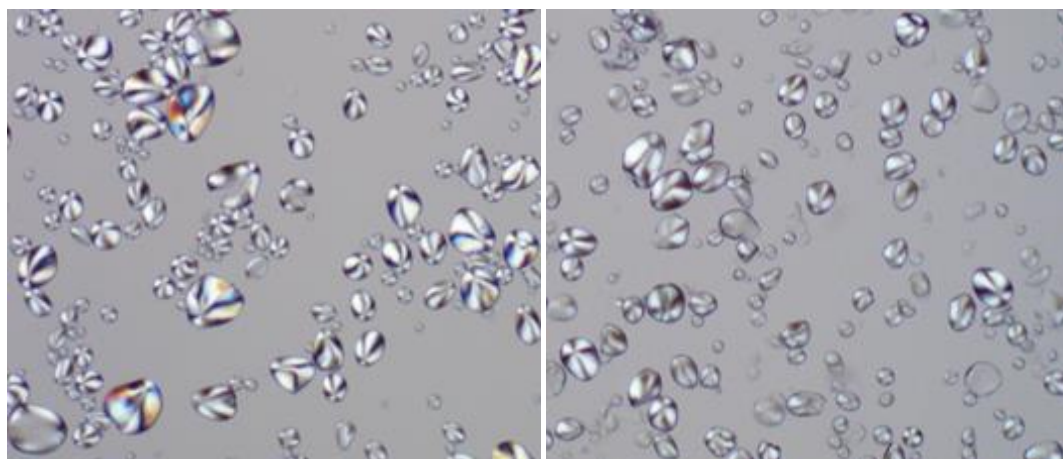


Figure 1: microscope images X85-0 (left) and X85-0.375 Bn (right) under polarized light; 100X

The DS and reaction efficiencies of all starches are displayed in Table 2. Only for DS-0.375 a reaction time of 96h was applied, the other reactions were finished after 72h.

Sample	DS <sup>a</sup> <sub>th</sub>	DS <sub>UV</sub>	Efficiency (%)
<b>W<sup>b</sup>-0.125</b>	0.125	0.10 ± 0.002	84
<b>W-0.25</b>	0.25	0.20 ± 0.004	81
<b>W-0.375</b>	0.375	0.29 ± 0.051	76
<b>PS-0.25</b>	0.25	0.22	88
<b>X115-0.375</b>	0.375	0.28	74
<b>X85-0.0027</b>	0.027	0.023	85
<b>X85-0.125</b>	0.125	0.09 ± 0.004	73
<b>X85-0.25</b>	0.25	0.19 ± 0.021	75
<b>X85-0.375<sup>c</sup></b>	0.375	0.25 ± 0.02	67
<b>X55-0.2</b>	0.2	0.16	79
<b>X55-0.3<sup>c</sup></b>	0.3	0.22	73

Table 2: reaction efficiency of benzylation of waxy potato starches.

<sup>a)</sup> Theoretical DS: moles benzyl chloride added per mole AGU.

<sup>b)</sup> Native waxy potato starch is indicated as 'W' and native 'regular' potato starch as 'PS'.

<sup>c)</sup> Some of the product dissolved during washing.

The reaction efficiencies are similar to values found in the literature [19,27], so the level of oxidation does not influence the efficiency of the benzylation reaction. During the reaction, samples were taken every 24 hours. The work-up procedure of these samples was similar as described above. Figure 2 shows typical DS build-in curves; both for native and oxidized base materials the progress was similar.

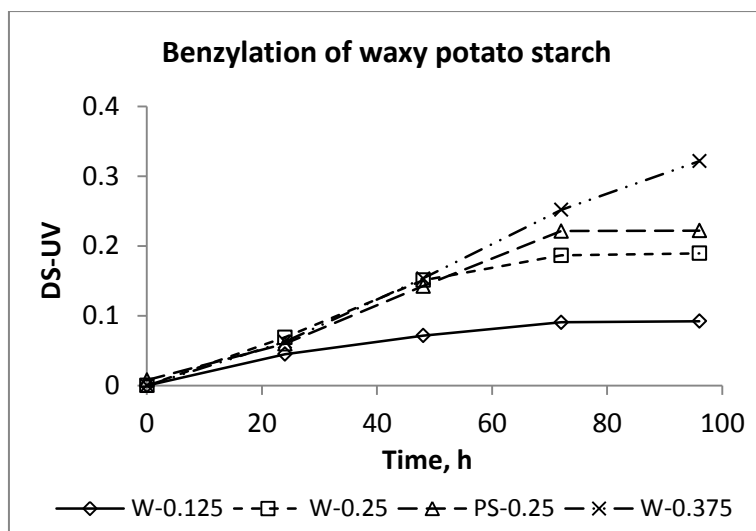


Figure 2: typical DS curve of different Benzylated starches.

The reaction kinetics appears pseudo-zero-order in benzyl chloride, which has limited solubility in water [23]. Cho & Lim [28] showed that the reaction rate depends on the NaOH concentration. During the reaction of DS = 0.125,  $[\text{OH}^-]$  is lower compared to reactions with a higher DS. Therefore, the reaction rate is lower. The other reactions proceed at a increasing  $[\text{OH}^-]$ , but in both the DS = 0.25 and 0.375 reaction, the total reaction rate is almost equal for 48h. So the total rate of reaction appears to be limited by the concentration of benzyl chloride in the continuous phase. Both effects can be observed in Figure 2.

### Rapid visco analysis

An RVA-profile reveals the pasting behavior of starch granules in suspension upon heating [43]. The granules will start swelling at the onset temperature, thereby increasing the viscosity of the suspension. At the peak viscosity, starch granules start to disintegrate and the starch will dissolve into the water phase. Although the starch granules may not completely disintegrate during an RVA measurement, due to lack of shear- and thermal input, an RVA profile provides useful information regarding the behavior of the product upon thermomechanical processing. The viscosity peak height may indicate possible processing problems upon cooking. The hot paste temperature is a measure for the starch solution viscosity just after processing and the set-back shows the increase of the solution viscosity when the paste cools down.

The results of the RVA measurements of all products are listed in Table 3. Native waxy potato starches show a decrease in the peak viscosity at increasing DS. The higher final viscosity of W-0.25 (625 mPa.s) compared to PS-0.25 (81 mPa.s), is explained by the absence of amylose, which has a lower molecular weight and thus a lower viscosity. The RVA profile of W-0.25 is very different from the oxidized starches, as can be seen in Figure 3. The decreased viscosity is explained by the formation of a dispersion [19,27]. Gelatinization proceeds slow and the viscosity increases well into the steady temperature period of 90 °C. The granules of W-0.375 Bn did not dissolve at all: merely deformed, amorphous (no Maltese cross under cross-polarized light), but distinct structures were observed. From Table 3 it can be observed that all derivatives from W-0 except W-0.375 have a decreased pasting-onset temperature compared to W-0, which is common for modified starches in general [44-46]: compare the onset temperatures of W-0 (72.8°C), X115-0, X85-0 and X55-0 (60.8 °C).

Sample	DS-th	P-onset (°C)	P-temp (°C)	Viscosity (mPa.s)				
				Peak	Hot paste	Final paste	Breakdown	Setback
<b>W<sup>a</sup></b>	0	72.8	83.6	2863	1350	1518	1513	168
<b>W<sup>a</sup></b>	0.125	71.4	59.9	1506	1468	1856	38	388
<b>W<sup>a</sup></b>	0.25	70.8	90.0	311	358	625	-47	267
<b>W<sup>a</sup></b>	0.375	79.6	90.0	20	11	6	9	-5
<b>PS<sup>a</sup></b>	0.25	72.1	90.0	32	52	81	-20	29
<b>X115</b>	0	70.0	78.7	2250	197	920	2053	723
<b>X115</b>	0.375	64.9	83.7	2660	215	17468	2445	17253
<b>X85</b>	0	65.6	72.5	602	65	256	537	191
<b>X85</b>	Control	62.3	74.1	787	40	164	747	124
<b>X85</b>	0.125	62.6	71.4	1410	47	173	1363	126
<b>X85</b>	0.25	61.2	72.1	1677	61	561	1616	500
<b>X85</b>	0.375	65.6	79.7	1250	78	5161	1172	5083
<b>X55</b>	0	60.8	66.1	211	26	84	185	58
<b>X55</b>	0.2	62.2	68.0	1152	28	168	1124	140
<b>X55</b>	0.3	52.8	75.4	435	33	733	402	700

**Table 3: RVA results**

<sup>a)</sup> The RVA profile of waxy potato starches were recorded at 5W%.

At increasing degree of benzylation, the decrease of the onset temperature is further enhanced in most cases, for example X85-0 (65.6 °C) vs. X85-0.25 (61.2 °C). However, if the hydrophobic content increases, for example for X85-0.375, the onset temperature increases again, which indicates a decreased tendency of the granules to dissolve. All measured onset temperatures were well above the reaction temperature. Moreover, oxidized and benzylated starches show a considerable increase

in the peak viscosity. To verify if the increase in peak viscosity was the result of hydrophobic content, a control experiment (without benzyl chloride) was performed with X85-0 as a starting material. As can be observed from Table 3, the RVA profile of X85-blanco does not show the increased peak viscosity, which gives reason to assume that the increased peak viscosity of benzylated and oxidized starches is caused by the benzyl-groups.

At  $DS_{th} > 0.3$ , the oxidized starches show a considerable increase in end-viscosity compared to their starting materials. The end-viscosity of these products was a function of the level of oxidation: a higher level of oxidation yielded a lower end-viscosity, as is illustrated in Figure 3.

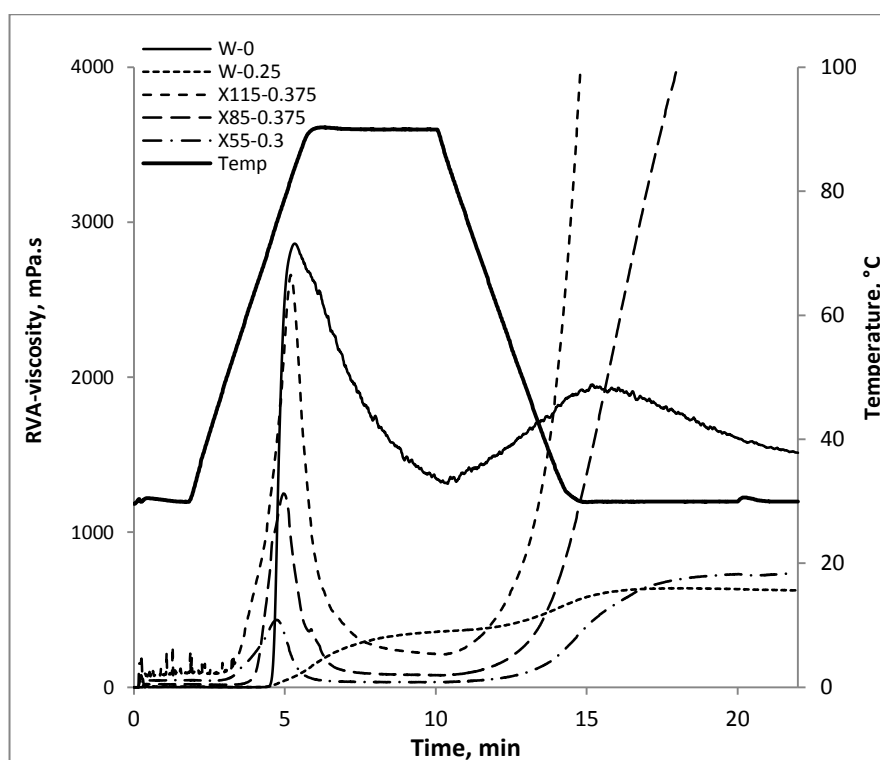


Figure 3: RVA recordings of benzylated starches.

Normally, such an increase is ascribed to retrogradation, a recrystallization process which causes a viscosity increase. Huijbrechts et. al [36], who modified native corn starch with Allyl Glycidyl Ether (AGE), observed a similar increase in final paste viscosity even without using degraded starch, and explained it by retrogradation. The cooked pastes of benzylated oxidized waxy potato starches, however, remained liquid, so apparently retrogradation was not believed to take place in this case. It is remarkable that for example X115-0.375 shows an enormous increase of the end-viscosity while the granules of W-0.375 do not disintegrate at all. This suggests that W-0.375 may be dissolved, but the viscosity difference between the starch gel-granule and the water is too large for complete

granular disruption. Another possibility is that the presence of carbonyl- and carboxyl groups from the oxidation process enhances solubilization.

### ***Cooked starch paste viscosity***

Figure 4-a shows the viscosity profiles of benzylated waxy- and normal potato starch. The solution texture of native waxy potato starch suggested incomplete granular disruption. Increased cooking time to 60 minutes did not change the profile. A DSC study by Thiewes and Steeneken [47] showed that at temperatures well above 100°C structural changes still occur. Other cooking methods, such as jet-cooking, improve gelatinization [18,27,48] but were not applied here. The viscosity of sample W-0.25 exceeded the viscosity of W-0 solution above a concentration of 8 W%, so the apparent decrease in viscosity suggested by the RVA measurement is only partly true. A sub-micron dispersion was formed by W-0.25, similar to PS-0.25, which is in agreement with known literature [18,19,27]. Due to the increased viscosity at increasing concentration and the presence of dispersed particles, it seems that at least part of the starch still dissolves, and that part also had a higher viscosity than native starch. Similar to the observations made during RVA measurements, the granules W-0.375 did not dissolve, despite a higher concentration (15 vs. 5 %W), longer cooking time and increased stirrer speed. Therefore, this product is not further taken into account.

The use of oxidized waxy potato starches as a base material for the benzylation reaction resulted in increased solubility of the products. The pastes obtained by cooking were not 'milky', but yellowish and slightly opaque. Unlike what was reported about degraded maize starch in the literature [27], no sub-micron dispersion was obtained, except occasional undissolved granule fractions were detected by light microscope. Figure 4 b-d show the viscosity profiles of oxidized and benzylated waxy potato starch products. The starting materials have decreased viscosity compared to W-0, due to degradation by the oxidation process. Decreased viscosity of the starting-material results in a decreased viscosity at a similar DS: X85-0.375 has a lower viscosity than X115-0.375. If the starting material is the same, however, the viscosity of the cooked starch dispersion depends strongly on the DS, as well as the concentration. This is best shown in Figure 4-b, where the viscosity of X115-0.375 exceeds the viscosity of X115-0 above 15 %W. Only X85-0.125 is lower than X85-0 over the whole measured concentration range. The other exception is X55-0.2 has a higher viscosity than X55-0 in the dilute region, but also the strong increase above 15 %W. This observation is left unexplained. All cooked benzylated starch products were stable at all concentrations, i.e. the

viscosity did not change over 24h, so no retrogradation occurred. The increase in viscosity is most pronounced at DS-th of 0.3 – 0.375. At high concentrations, the increase in viscosity sometimes exceeds 2 orders of magnitude compared to the starting material while at low concentrations the viscosity is lower. For example, the viscosity of X115-0 increases from 100 mPa.s. at 10 %W to approximately 3000 mPa.s at 25 %W while X115-0.375 increases from 13 to 200.000 mPa.s over the same range.

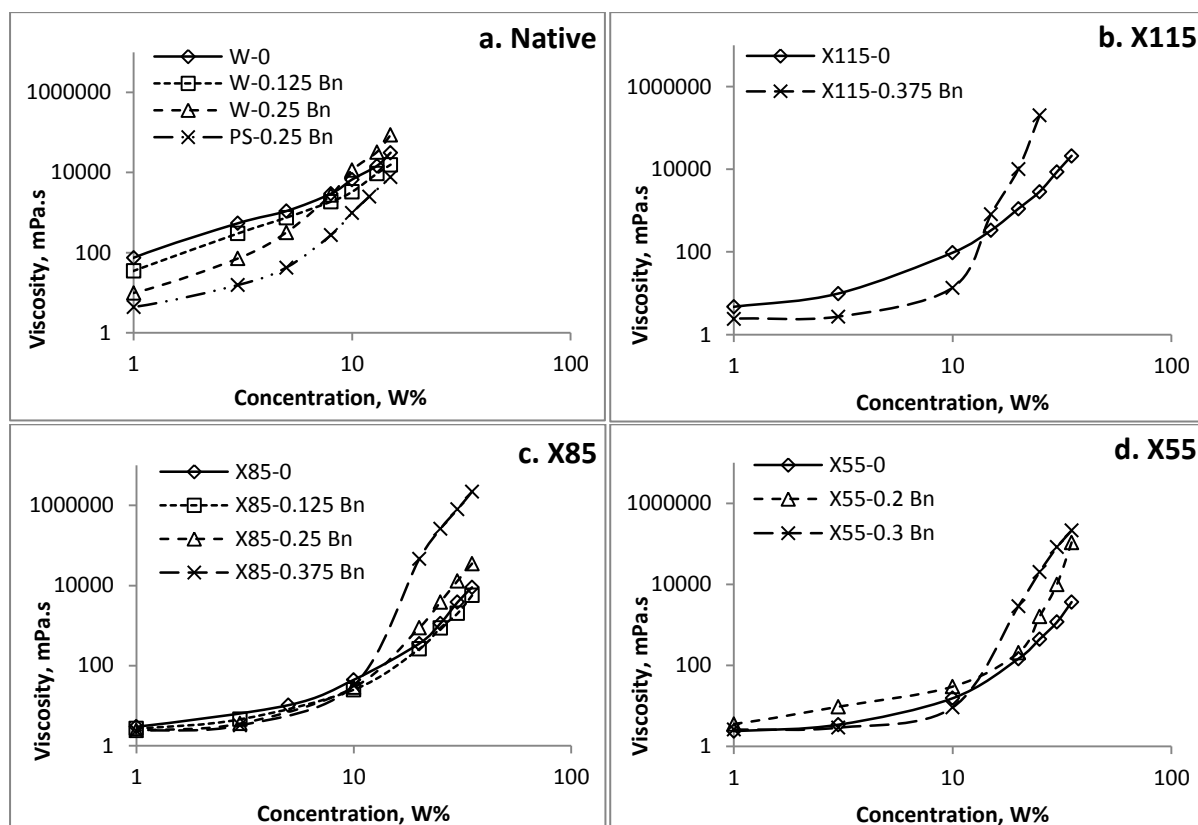


Figure 4: typical examples of concentration-viscosity behavior of benzylated starches <sup>a)</sup>.

<sup>a)</sup> X115-0.375 at 25% was extrapolated; at 2 s<sup>-1</sup> the rheometer was operating at maximum torque.

The large viscosity increase may be explained by hydrophobic interactions of the benzyl groups. It is known that hydrophobic groups, substituted on a water soluble polymer, introduce new rheological properties to the product; one of the possibilities being increased viscosity [31,49]. The new rheological behavior is a function of the substitution pattern on the polymer backbone; random or block-wise. Block-size and relative hydrophobicity of the substituent contributes to the magnitude of hydrophobic interaction. In the dilute regime, hydrophobic blocks cause aggregates, which decrease the hydrodynamic volume of the molecules and hence the viscosity. Above a critical concentration the aggregates become interconnected and a three dimensional network is formed,

resulting in a large viscosity increase [50,51]. In starch chemistry it is well accepted that reaction takes place in the amorphous parts of the starch granules (i.e. near 1-6 linkages) [52], which suggests that a 'block like'- rather than a random substitution pattern of benzyl groups seems more likely to have formed during the reaction. Moreover, it seems logical to assume that the viscosity increase of oxidized starches also occurs for native starches. It is strange, therefore, that both normal and waxy potato starch with DS-th = 0.25 form a dispersion and not a 'very high' viscous gel, as observed by Huijbrechts et al. [53] who substituted allyl glycidyl ether on corn starch.

Pyrene UV emission measurements revealed hydrophobic interactions between the benzyl groups in the starch solutions. In addition, the molecular weight distribution, determined by GPC measurements, show that the changes in viscosity are too large to be accounted for by the increase of molecular weight due to addition of benzyl groups alone, see Table 4. It can be observed that the molecular weight of the control experiment products decreases by about 20%. After benzylation, the decrease is less. In fact, only at a DS-th of 0.375 the molecular weight of X85 increases by 11% while it should have increased by about 20% if no degradation would take place. Another explanation of the increased viscosity could be the formation of amylose-lipid complexes, which may also be formed by potato starch amylopectine due to its fine-structure [54-56], but these were not determined here.

<b>Starch</b>	<b>M<sub>w</sub> (10<sup>6</sup>)</b>
<b>X85-0</b>	2.60 ± 0.17
<b>X85-BI-R</b>	2.09 ± 0.02
<b>X85-0.125</b>	2.52 ± 0.08
<b>X85-0.25</b>	2.13 ± 0.09
<b>X85-0.375</b>	2.89 ± 0.11

**Table 4: molecular weight distribution of Benzylated X85 products**

### ***Effect temperature***

To the best of our knowledge, the viscosity as a function of temperature of benzylated starches has not been reported in the literature before. Amphiphilic polymers are known to display peculiar thermo responsive rheological behavior due to a shift in the balance between polar and disperse forces [31,57]. This may result in the introduction of an upper- or lower critical solution temperature (UCST/LCST), which results in a sudden change in viscosity at increasing temperature. Usually, a liquid or solution shows a gradual decrease in viscosity if the temperature increases. Figure 5 shows the viscosity as a function of temperature for the products based on X85. Other products showed similar thermal behavior, except for W-0 and W0.125 which showed little temperature dependence.

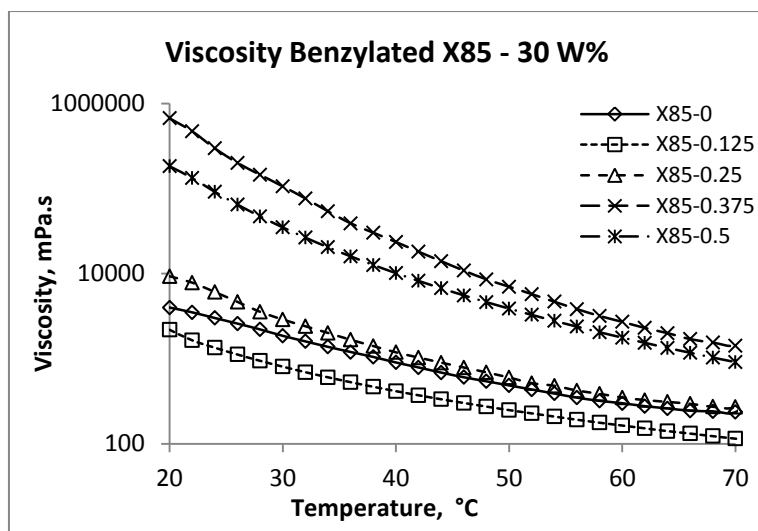


Figure 5: typical temperature profiles of benzylated waxy potato starch products.

All temperature profiles could be modeled by the Andrade relation (Equation 4), which is basically an Arrhenius type equation [58].

$$\log(\eta) = A + \frac{B}{T} \quad (\text{Equation 4})$$

Here, T is the absolute temperature, in K. The term B represents the activation energy; the force needed to increase Brownian motion of molecules. A is a pre-exponential factor.

Starch	DS <sub>Bn</sub>	$\eta$ - 30 % <sup>a</sup> mPa.s (10 <sup>3</sup> )	-A	B	R <sup>2</sup>
Waxy	0	31.3 <sup>b</sup>	-1.04	880	0.998
Waxy	0.125	15.7 <sup>b</sup>	-1.05	840	0.994
Waxy	0.25	32.7 <sup>b</sup>	8.44	3790	0.984
Potato	0,25	2.5	2.45	1650	0.990
X115	0	8.6	3.56	2310	0.999
X115	0.375	10.2 <sup>c</sup>	6.54	2840	0.987
X85	0	3.8	5.93	2790	0.999
X85	0.125	2.0	4.38	2240	0.998
X85	0.25	13.0	8.32	3570	0.996
X85	0.375	717.3	13.41	5590	0.999
X85	0.5	175.9	8.78	3790	0.962
X55	0	1.2	6.55	2800	0.997
X55	0.2	10.0	9.28	3950	0.999
X55	0.3	82.7	12.45	5030	0.994

Table 5: Andrade coefficients of starch solutions and viscosity at 30W%

<sup>a)</sup> Viscosity at 20°C

<sup>b)</sup> Viscosity at 13 %W

<sup>c)</sup> Viscosity at 20 %W



The profiles of all products could be fitted by the Andrade model. This suggests the starch dispersions show normal thermo-rheological behavior and that in the reported range the nature of the dispersion is unchanged; i.e. the amount of dissolved material remains the same. Table 5 shows the Andrade parameters of the measured starch dispersions; only 30 %W concentrations are displayed. W-0, W-0.125 and X115-0 deviate from the general correlation between A and B [58] but showed a reasonable fit. Based on the above, it was concluded that the benzylated starch solutions did not show thermo responsive behavior. Instead, normal behavior for dissolved polymers was observed.

### ***Dry starch film surface tension***

The film surface tension of W-0 was determined as 56.9 mN/m, which is in agreement to the values found in the literature. Bengtsson et. al. reported a surface tension of around 50 mN/m for normal potato starch. A value of around 60 mN/m was reported for maize starch by Angellier et. al. [59] and by Thielemans et. al. [60]. The surface tension values, the work of adhesion and the work of separation in water are listed in Table 6 for all products.

Although the surface tension of oxidized starches remains approximately 56 mN/m, the contribution of polar forces to the surface tension seems to increase at increased degree of oxidation, but the X55-0 deviates from this trend. Upon benzylation, the total surface tension of the films of all products decreases and the relative contribution of dispersive forces increased, especially for the native starch products. W-0 had a contribution of polar forces of 31.7 mN/m which dropped to 9.2 mN/m for W-0.25. In addition, the film surface tension of the products approaches 45 mN/m upon benzylation. This value approaches 43.1 mN/m, which is the surface tension measured for Styronal D517, a commercially available SBR latex from BASF applied in paper coatings by the paper industry, here used as a reference. At similar DS, but different levels of oxidation (molecular weight), the surface tension of starch films are comparable which is in agreement with the literature [40]. If  $W_{adh}$  is calculated according to Equation 1 for starch-cellulose as well as starch- $CaCO_3$ , it is found that the interaction reduces as DS increases. This means that it will take less energy to separate the two compounds. Furthermore, Equation 2 was used to calculate  $W_{adh}$  in case of submerging the composite in water. The calculation shows that spontaneous separation will occur in all cases ( $W_{adh} < 0$ ), however, the water sensitivity decreases considerably as DS-Bn increases. Note that some starches, with respect to surface properties, show very similar results compared to Styronal D517.

Low water sensitivity is important since water is used to cover areas not to be covered by ink during off-set printing. Repeated contact with water may cause migration of starch, which is undesirable.

Starch-sample	$\gamma^D$	$\gamma^P$	$\gamma^T$	$R^2$	St-Cell <sup>b</sup>	St-CaCO <sub>3</sub>	Cell.sep	CaCO <sub>3</sub> sep
W-0	25.3	31.7	56.9	0.998	112.5	213.7	-99.5	-176.6
W-0.125	31.0	16.1	47.1	0.850	105.2	181.6	-84.1	-136.2
W-0.25	36.1	9.2	45.3	0.957	102.3	163.8	-73.0	-110.3
A-0.25	37.9	7.0	44.9	0.912	100.8	156.4	-67.8	-99.1
X115-0	24.8	31.8	56.0	0.990	111.9	213.2	-99.6	-176.6
X115-0.375	27.7	17.3	45.0	0.976	102.6	180.7	-82.8	-136.6
X85-0	21.7	35.1	56.8	0.999	110.3	215.5	-98.2	-179.2
X85-0.125	31.4	16.9	48.3	0.908	106.5	184.6	-85.9	-139.6
X85-0.25	29.2	17.2	46.4	0.902	104.3	182.5	-84.2	-138.2
X85-0.375	30.3	14.7	45.0	0.944	102.9	176.2	-80.6	-129.7
X55-0	26.7	24.4	51.1	0.943	108.2	198.7	-92.5	-158.7
X55-0.2	30.9	13.0	44.9	0.886	101.6	171.4	-76.7	-122.2
X55-0.3	29.6	15.0	44.5	0.912	102.4	176.3	-80.6	-130.2
Styronal D517	23.0	20.1	43.1	0.950	99.5	181.9	-81.9	-139.9

Table 6: surface tension components of benzylated waxy potato starch products and calculated  $W_{adh}$  for various systems.

<sup>a)</sup> The surface tension is reported in mN/m for all values.

<sup>b)</sup> St-Cell and St-CaCO<sub>3</sub> represent  $W_{adh}$  for starch-cellulose and starch-CaCO<sub>3</sub>. Cell-sep and CaCO<sub>3</sub>-sep represent the work of separation in water for these systems. Values for the surface tension of cellulose, CaCO<sub>3</sub> and water were obtained from the literature for disperse (d), polar (p) and total (t). Cellulose (40, 18.8, 58.8 mN/m) from [61,62], CaCO<sub>3</sub> (54.5, 153.4, 207.9 mN/m) from [63] and water (21.8, 51, 72.8 mN/m) from [40].

## Conclusion

A range of benzylated potato starches based on waxy potato starch was prepared and characterized. The effect of the level of oxidation and DS on starch properties upon benzylation was studied. Industrial grades of oxidized waxy potato starch were used for this purpose. The reaction efficiency of benzylation was not influenced by the degree of oxidation and was comparable to values found in the literature with respect to normal potato starch and corn starch. An increase of RVA peak viscosity was observed which was assigned to the presence of hydrophobic groups. Native, benzylated waxy potato starch behaved similar to what was described in the literature regarding benzylated normal potato starch; it only had a higher viscosity. A significant viscosity increase was found for oxidized starches at DS > 0.3. By varying the degree of oxidation and DS-Bn, the viscosity and hydrophobic content of the starch solution can be tuned, which could be beneficial for the

paper coating process. Benzylated oxidized starches did not form dispersions like the native benzylated starches upon cooking. This can be explained by either the decreased molecular weight of oxidized starches or by the presence of carbonyl- and carboxyl groups in oxidized starch. The relatively small increase of the molecular weight, determined by GPC, and the peak shift in the pyrene emission spectrum indicated that the increased viscosity is most likely the result of hydrophobic interactions. Amylose-lipid complex formation was not measured but may also contribute to the total viscosity. No thermosresponsive rheological effects were detected. The starch film surface tension decreased at increasing DS and the contribution of polar forces to the total surface tension decreased as expected. It was calculated that the water sensitivity decreased as well. The results suggest that benzylated starches based on oxidized waxy potato starches should, at least partly, be able to replace SBR in paper coatings. Further research will focus on this subject.

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